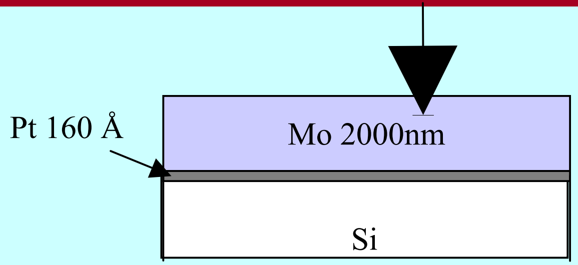
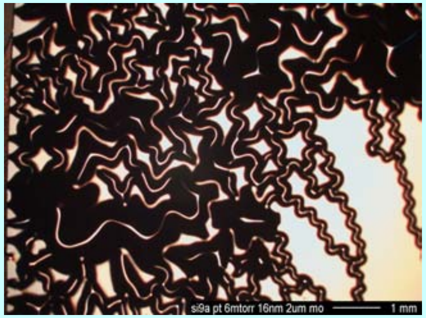
Degradation Mechanisms, Micromechanics and Microstructural Engineering of High Permittivity Thin Film Capacitor Materials



Controlling Adhesion of Pt to Oxide Surfaces

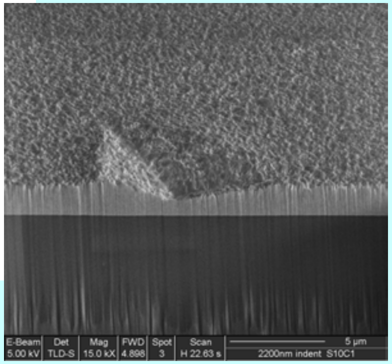
Driving force for delamination of Pt/SiO_2 interface controlled by residual compressive stress in Mo overlayer and by indentation.

6 mTorr Ar/*weak interface*

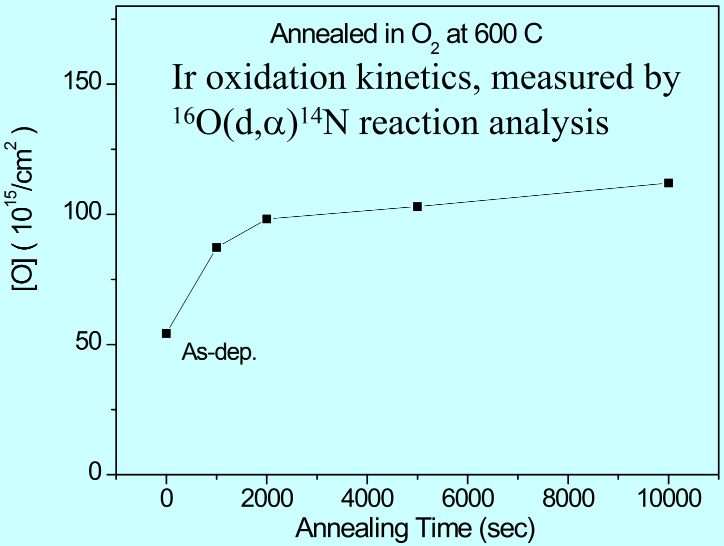


At high Ar pressures spontaneous telephone-cord delaminations are observed.

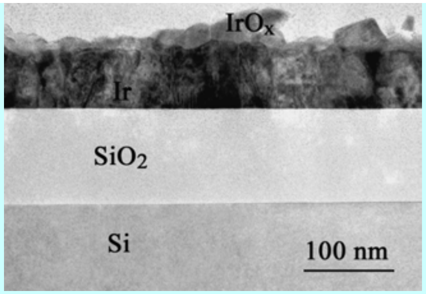
3 mTorr Ar/*strong interface*

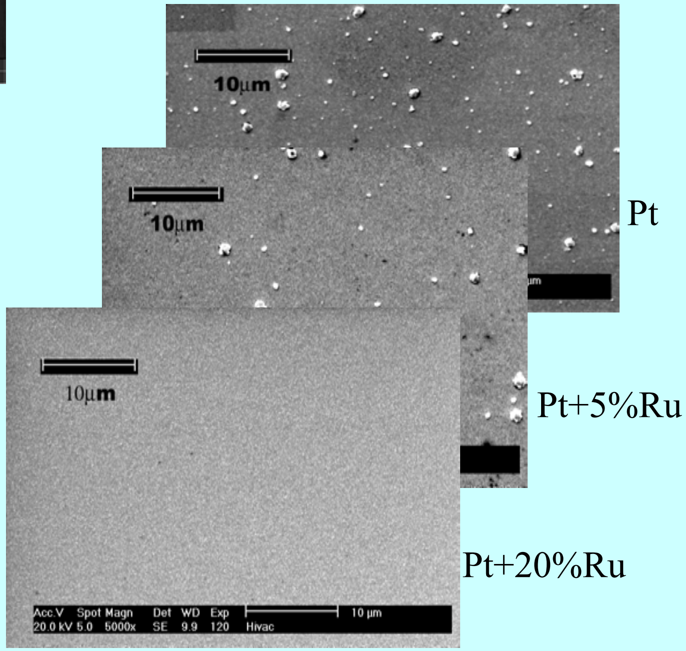


At low Ar pressures,atomic shot peening by Ar neutrals created in sputtering dramatically improve adhesion.



Conformal IrO_x layer formed during oxidation of Ir in O_2 at 600°C





Materials Science/ Degradation Mechanisms, Micromechanics and Microstructural Engineering of High Permittivity of Thin Film Capacitor Materials; P.C. McIntyre et al./Stanford University; DMR-0072134 (GOALI-Focused Research Group). We are studying the adhesion of electrode materials with the substrates and other layers that are expected to be used to integrate high-K dielectrics such as (Ba, Sr)TiO_3 (BST) and Pb(Zr,Ti)O_3 into Si-based semiconductor devices. We are developing an adhesion test based on nanoindentation-induced delamination, using a compressively stressed Mo overlayer film to produce a large driving force for delamination. In recent experiments we have discovered that the adhesion of Pt to SiO2 depends very sensitively on the Ar pressure used during sputtering. For Pt deposited at an Ar pressure of 6mTorr, telephone-cord blisters occur spontaneously a few hours after film deposition. For Pt films deposited at an Ar pressure of 3mTorr, no such spontaneous delaminations are observed. Even after nanoindentation has caused the Si substrate to crack, the interface does not delaminate. We believe these dramatic effects are caused by the effects of atomic shot peening by neutral Ar atoms created in the sputtering process. At low Ar pressures, highly energetic neutrals are believed to collide with the interface as it is being created. The atomic mixing in that process greatly improves the adhesion.

Research in this program has also included studies of thermal stability and oxidation of Ir-based thin film electrodes. While annealing in an oxygen ambient, we observed two dominant phenomena: grain growth and the oxidation of Ir films. Significant oxidation of the Ir films is found to occur at temperatures of 600°C and higher. As a result, many extrusions were created on the surface of the Ir film with dimensions at 700°C of about 0.5 um in width and 0.3 um in height (for a sample with 100 nm average Ir film thickness). Cross-section TEM images (an example is shown on this slide) of oxidized Ir films also show the formation of a relatively uniform surface oxide layer across the majority of the film surface. The nucleation and growth mechanism of the extrusions and possible competition with the more uniform oxidation process are now under investigation. The kinetics of surface oxidation of Ir films were probed by accelerator-based nuclear reaction analysis at Los Alamos National Laboratory. The $^{16}O(d,\alpha)^{14}N$ nuclear reaction spectra obtained give the areal density of oxygen in the 10 – 40 nm thick layer near the Ir film surface, and this increases with annealing time in oxygen at 600°C. Our preliminary results suggest that the kinetics of Ir oxidation exhibit a logarithmic rate law (as shown on the slide). This is the first systematic study of the early stages of Ir oxidation.

Lehigh's (subcontract PY-0826) specific contribution to the program is to determine the benefits of solid solution strengthening on electrode behavior. The beneficial effect of solid solution alloying on high temperature strength reported in the literature for bulk materials raises the possibility that similar gains may be realized in thin film metals. In addition, alloying could result in certain ancillary improvements in behavior such as increased adhesion or decreased diffusion of oxygen and barrier materials. This approach would require very little change in current electrode processing methods and could reduce cost compared to pure Pt electrodes.

We have demonstrated for the first time that solid solution alloying over a wide range of compositions can have a significant beneficial effects on the strength and hillocking behavior of thin metal films. Although not shown on this slide, we have also developed a model that matches well with experimental room temperature flow stress data. In addition, we have shown that proximity of a nanoindenter tip to a grain boundary has a large effect on discrete dislocation behavior during loading. This explains the discrepancies often observed in indentation of small-grain and large-grained films.